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(72) (75)	Inventor; and Inventor/Applicant (for US only): SLOMAN, Rog [GB/GB]; Advanced Composites Group Ltd., Ct House, Adams Close, Heanor Gate Industrial Est byshire DE75 7SW (GB).	omposi	tes	With international search report.					
(74)	Agent: CAMPBELL, Iain, Angus; Swindell & Per Friar Gate, Derby DE1 1GY (GB).	arson,	48						
(54)	Title: IMPROVEMENTS IN OR RELATING TO COMPOSITE COMPONENTS	O PRI	ESS	URE TRANSMITTERS FOR USE IN THE PRODUCTION OF					
(57)	Abstract								
note	- 1 is formed from a symble electromeric material W	hich is for ex	s na	onents may take the form of a caul plate, pressure intensifier or vacuum artially cured, normally when supported on a mould, at a temperature ple 175 °C, while unsupported. It may incorporate a reinforcing layer					

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# Improvements in or relating to pressure transmitters for use in the production of composite components

This invention relates to pressure transmitters for use in the production of composite components. The term "pressure transmitter" as used herein is intended to refer to cover members and ancillaries used to allow pressure to be applied to composite components during their moulding in a tool. The expression includes caul plates, pressure intensifiers and reusable rubber bags.

The use of caul plates, pressure intensifiers and rubber bags to produce smooth surfaces on composite components is a normal practice. Caul plates and/or pressure intensifiers can be made from an elastomeric material and enable appropriate pressure to be applied to the laminate in order to provide a relatively smooth surface on the bag side. In the case of pressure intensifiers, these are mainly used in female features on the non moulded side of the component. The caul plates consist of an elastomeric sheet which may be reinforced by a resin pre-impregnated fibre. The disadvantage of these caul plates made from fully formulated sheet rubber is that they require to be cured at high temperatures (greater than 100°C). Also, some reinforced caul plates exhibit the disadvantage that the elastomeric material tends to separate from the fibre reinforcement, and others may give undesirable contamination problems.

As used herein, the expression "partially cured" when referring to a curable component means cured to the extent that the component can be removed from a mould, tool or former (which may or may not have high temperature capability (ie being capable of withstanding temperatures of greater than 100°C)), and then be handled and further processed (including a higher temperature further curing stage) without causing damage to the component. Further the expression "elastomeric material" includes the precursors of such materials, for example, fully formulated polymeric materials which after partial or full cure exhibit elastomeric properties. The polymeric material may be in sheet form.

According to a first aspect of the present invention there is provided a pressure transmitter comprising an elastomeric material which is partially or at least partially cured at a temperature not exceeding 100°C.

According to a second aspect of this invention, there is provided a pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a reinforcement and an outer region of an elastomeric material, the elastomeric material being partially or, at least partially, curable at a temperature not exceeding 100°C.

Preferably, the elastomeric material is partially or, at least partially, curable at 20 - 70°C, preferably 65°C. Conveniently the elastomeric material is partially cured during a period of 14 hours.

Desirably, the elastomeric material is further cured at an elevated temperature to reach a state of being substantially fully cured. Preferably the elevated temperature lies in the range 170 - 185°C. Preferably, the elastomeric material can be further cured at a temperature of substantially 175°C. Conveniently the elastomeric material is further cured for a period of at least 2 hours.

Preferably elastomeric material is a silicone elastomer, an acrylate or a fluoroelastomer.

According to a further aspect of this invention, there is provided a pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a curable reinforcement and an outer region of elastomeric material, the curable reinforcement comprising resin pre-impregnated onto fibres, said resin being partially, or at least partially, curable at 100°C or less.

Preferably the elastomeric material cures or at least partially cures at a temperature greater than the cure or partial cure temperature of the curable

reinforcement. This provides the advantage that the resin cures or partially cures before the elastomer, thereby reducing shrinkage of the elastomer.

Preferably, the elastomeric material is partially, or at least partially, cured at a temperature in the range of 20 - 70°C more preferably at 65°C. Preferably, the elastomeric material is partially cured during a period of 14 hours.

Desirably the elastomeric material is further cured to reach a state of full cure at a temperature in the range of 170 - 185°C. Preferably, the elastomeric material can be further cured at a temperature of substantially 175°C. Conveniently the elastomeric material is further cured during a period of 2 hours.

According to a still further aspect of this invention, there is provided a pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a curable prepreg reinforcement and an outer region of an elastomeric material, the curable prepreg reinforcement being in the form of resin pre-impregnated fibres defining a plurality of interstitial spaces, wherein the elastomeric material of the outer region substantially fills the interstitial spaces.

This has the advantage that the elastomer is keyed to the fibres, thereby mitigating any separation of the resin pre-impregnated fibres from the elastomer.

Preferably, the pressure transmitter is in the form of a caul plate, or a pressure intensifier for use in applying pressure to surfaces of a moulded component. The invention is particularly suitable for use with moulding techniques which involve the use of a bag applied to the moulding, for example by using vacuum bags.

According to another aspect of this invention, there is provided a method

of curing a pressure transmitter, comprising providing a pressure transmitter as described above, and thereafter at least partially curing the pressure transmitter at a temperature not exceeding 100°C.

The pressure transmitter may be partially or, at least partially, cured at a temperature in the range of 60 - 70°C (approximately 140 - 160°F), more preferably at 65°C (approximately 150°F). Conveniently, the pressure transmitter is partially cured during a period of at least substantially 14 hours. The pressure transmitter may be partially cured within 14 hours.

Desirably, after said partial or, at least partial, curing, the pressure transmitter is further cured at a temperature in the range of 170 - 185°C (approximately 340 - 365°F). Preferably, the pressure transmitter is further cured at a temperature of substantially 175°C (approximately 350°F). The pressure transmitter may be so further cured during a period of at least substantially 2 hours. The pressure transmitter may be so further cured within 2 hours.

The elastomeric material may be a silicone elastomer.

By appropriate selection of the resin and elastomeric material, the low temperature curing of the pressure transmitter will result in the resin curing or, partially curing, before the elastomer has fully cured. This has the advantage of minimising shrinkage of the elastomer. Another advantage of the low temperature curing (ie less than 100°C) is that it can take place on a tool that can only withstand such low temperatures. The step of further curing the pressure transmitter provides the elastomeric material with the properties to enable the pressure transmitter to perform its function.

An embodiment of the invention will now be described by way of example only with reference to the accompanying drawings in which:-

Fig. 1 shows a schematic diagram of a pressure transmitter in the form

of a caul plate in use;

Fig. 2 shows a schematic diagram of a pressure transmitter in the form of a pressure intensifier in use;

Fig. 3 shows a reinforcement not to scale with resin pre-impregnated fibres defining interstitial spaces; and

Fig. 4 is a view similar to Fig. 3 but showing an elastomer in the interstitial spaces.

Referring to Fig. 1, there is shown a prepreg lay-up 10 to be used in forming a composite component. The prepreg lay-up is arranged on a tool 12 with a caul plate 14 placed on the lay-up 10. The caul plate 14 comprises an inner region 16 of a fibre reinforcement and an outer region 18A,18B of an elastomeric material 18. In the formation of the composite component, a vacuum bag or sheet 19 is arranged over the lay-up 10 and the caul plate 14. Air is removed from the vacuum bag 19 whereby air pressure provides the necessary pressure for moulding and heat is also applied, in the standard way.

The fibre reinforcement 16 comprises woven fibres 20 defining a net like structure having interstitial spaces 22 (see Fig. 3). The interstitial spaces 22 are, as shown in Fig. 4, filled with the elastomeric material 18 defining outer regions 18A,18B. The reinforcement 16 may be formed of one or a plurality of layers of the woven fibres 20.

The caul plate 14 is first processed to make it usable as described in the preceding two paragraphs by partially curing the caul plate 14 at a temperature of less than substantially 65°C at least 14 hours during a first curing stage the caul plate being supported on a mould which need not be capable of withstanding high temperatures (eg above 100°C) during the process. This first curing stage partially or fully cures the resin and partially cures the

elastomeric material 18. This minimises the shrinkage of the elastomeric material 18. After the first curing stage, the caul plate 14 is then further cured during a second curing stage for at least 2 hours at a temperature of substantially 175°C to fully cure the resin and the elastomeric material such that the caul plate 14 develops the appropriate properties normally expected of a caul plate 14 (see below). This second stage does not necessarily require the use of a mould to support the caul plate.

Thus, the resin and elastomeric material are selected to be capable of partial curing at low temperature ie less than 100°C.

As can be seen at Fig. 1 a wrinkle 24 in the prepreg lay-up 10 can be formed where adjacent plies overlap and at other places. The use of a caul plate 14 assists in smoothing out or preventing the formation of such wrinkles 24.

The caul plate may have a microporous membrane 118 arranged on its side adjacent the lay-up 10 to facilitate removal of gases emitted by the resin during the curing process. Alternatively a solid inpermeable sheet for example of HALAR could be substituted for the microporous membrane. The sheet may be in the form of a film bonded to the caul plate.

Referring to Fig. 2, there is shown a tool 12 at a corner region 22 thereof where the prepreg lay-up 10 defines a concave region 24. A pressure intensifier 26 is arranged in the concave region 24 to ensure that appropriate pressure is applied thereto.

The pressure intensifier 26 is formed in a similar manner to the caul plate described above using similar cure and postcure temperatures.

In a modification the reinforcement may be omitted from the caul plate or from the pressure intensifier. In the modification, the caul plate and pressure intensifier are manufactured in the manner described above, that is they are partially cured at a temperature not exceeding 100°C on a mould which

need not be capable of withstanding temperatures of greater than 100°C so that it can be manufactured, for example, from wood, plaster or other suitable easily worked material but after the initial cure stage the caul plate and pressure intensifier is removed from the mould for further curing to a fully or approaching fully cured state at an elevated temperature for example 175°C. As before the initial cure time can be 14 hours and the postcure time 2 hours.

In a further modification of the present invention the pressure transmitter may take the form of a vacuum bag, that is a bag formed, in the simplest example, from two sheets of elastomeric material, sealed or sealable around the periphery of the sheets to form a bag which, after fitting with normal backing connections etc. be used in a vacuum bag moulding process. In this modification, as before, the vacuum bag is formed from two sheets of fully formulated polymeric material which are made into the bag when the material is in an uncured state (examples of suitable material being set out below). The bag can be cured during the initial cure stage which is carried out, for example for 14 hours, at temperatures no greater than 100°C and typically 65°C, thereafter, as appropriate, the bag can be fully cured bearing, for example, a further 2 hour cure cycle at an elevated temperature for example 175°C. Standard vacuum bag fitments for example vacuum terminals, openable seals etc. can be fitted before the initial cure or if convenient before the postcure, that is after the initial cure.

Examples of the properties of suitable elastomeric materials 18 are set out below.

#### Example 1

#### **Physical Properties**

Form:

soft and conformable with the slightest degree of

tack.

Color:

royal blue

SUBSTITUTE SHEET (RULE 26)

Thickness:

0.060", (60mils), other thickness will be available.

Width:

up to 50", calendered rolls.

### **Cured Properties**

**Durometer** 

70 (nominal)

Tensile Strength

1000+(psi)

Elongation at Break

350+(%)

Modulus at 100%

505 (psi)

Modulus at 300%

940 (psi)

Tear Strength

160+(ppi)

**Compression Set** 

30 (%) (22 hours at 350°F)

Adhesion

excellent (cocured to LTM prepreg)

Temperature Resistance

450°F to 500°F (when fully cured)

### Example 2

#### **Physical Properties**

Form:

soft and conformable with the slightest degree of

tack.

Color:

clear

Thickness:

0.085", (85mils), other thickness will be available.

Width:

up to 50", calendered rolls.

#### **Cured Properties**

Durometer

40 (nominal)

Tensile Strength

1510+(psi)

**Elongation at Break** 

925+(%)

Modulus at 100%

300 (psi)

Modulus at 300%

300 (psi)

Tear Strength

150+(ppi)

SUBSTITUTE SHEET (RULE 26)

**Compression Set** 

TBD

Temperature Resistance 450°F to 500°F (when fully cured)

Various modifications can be made without departing from the scope of the invention.

#### **CLAIMS**

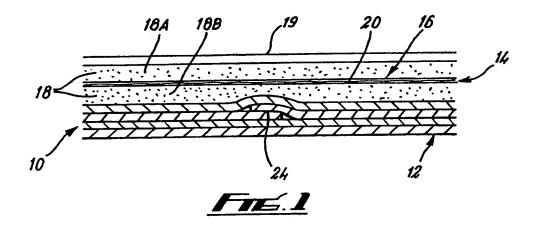
- 1. A pressure transmitter comprising an elastomeric material which is partially or at least partially cured at a temperature not exceeding 100°C.
- 2. A pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a reinforcement and an outer region of an elastomeric material, the elastomeric material being partially or, at least partially, curable at a temperature not exceeding 100°C.
- 3. A pressure transmitter as claimed in claim 1 or claim 2, wherein the elastomeric material is partially or, at least partially, curable at 20 70°C.
- 4 A pressure transmitter as claimed in claim 3 wherein the elastomeric material is partially or, at least partially, curable at 65°C.
- 5. A pressure transmitter as claimed in claim 3 or claim 4, wherein the elastomeric material is further cured to reach a state of being substantially fully cured at a temperature of at least 170°C.
- 6. A pressure transmitter as claimed in claim 5, wherein the elastomeric material is further cured to reach a state of being substantially fully cured at a temperature of 175°C.
- 7. A pressure transmitter as claimed in claim 3 or claim 4, wherein the elastomeric material is partially cured during a period of 14 hours.
- 8. A pressure transmitter as claimed in claim 5 or claim 6, wherein the elastomeric material is further cured for a period of at least 2 hours.
- 9. A pressure transmitter as claimed in any one of the preceding claims, wherein the elastomeric material is a silicone elastomer, an acrylate or a

fluoroelastomer.

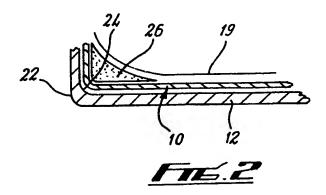
- 10. A pressure transmitter as claimed in any of claims 2 to 9, wherein the resin material is curable at a temperature not exceeding 100°C.
- 11. A pressure transmitter as claimed in any one of claims 2 to 10, wherein the curable prepreg reinforcement in the form of resin pre-impregnated fibres defining a plurality of interstitial spaces, wherein the elastomeric material of the outer region substantially fills the interstitial spaces.
- 12. A pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a curable reinforcement and an outer region of elastomeric material, the curable reinforcement comprising resin pre-impregnated onto fibres, said resin being partially, or at least partially, curable at a temperature not exceeding 100°C.
- 13. A pressure transmitter as claimed in claim 12, wherein the elastomeric material cures or at least partially cures at a temperature greater than the cure or partial cure temperature of the curable reinforcement.
- 14. A pressure transmitter as claimed in claim 13, wherein the elastomeric material is partially, or at least partially, cured at a temperature in the range of 20 70°C.
- 15. A pressure transmitter as claimed in claim 14, wherein the elastomeric material is partially, or at least partially, cured at a temperature of 65°C.
- 16. A pressure transmitter as claimed in any of claims 13 to 15, wherein the elastomeric material is partially cured during a period of 14 hours.
- 17. A pressure transmitter as claimed in any of claims 13 to 16, wherein the elastomeric material is further cured to reach a state of full cure at a temperature of at least 170°C.

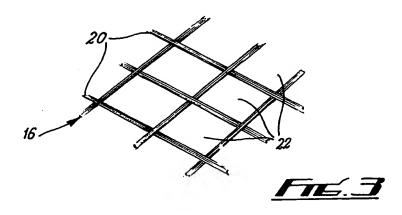
- 18. A pressure transmitter as claimed in claim 17, wherein the elastomeric material is further cured to reach a state of full cure at a temperature of 175°C.
- 19. A pressure transmitter as claimed in claim 17 or claim 18, wherein the elastomeric material is further cured during a period of 2 hours.
- 20. A pressure transmitter for use in the production of composite components, the pressure transmitter comprising an inner region of a curable prepreg reinforcement and an outer region of an elastomeric material, the curable prepreg reinforcement being in the form of resin pre-impregnated fibres defining a plurality of interstitial spaces, where in the elastomeric material of the outer region substantially fills the interstitial spaces.
- 21. A method of curing a pressure transmitter comprising providing a pressure transmitter as claimed in any one of the preceding claims, and thereafter at least partially curing the pressure transmitter at a temperature not exceeding 100°C while supported on a mould which need not be capable of withstanding temperatures of greater than 100°C.
- 22. A pressure transmitter substantially as hereinbefore described with reference to Fig. 1 or Fig. 2 or Figs. 3 and 4 of the accompanying drawings.
- 23. A method of curing a pressure transmitter substantially as hereinbefore described.
- 24. Any novel subject matter or combination including novel subject matter disclosed herein, whether or not within the scope of or relating to the same invention as any of the preceding claims.

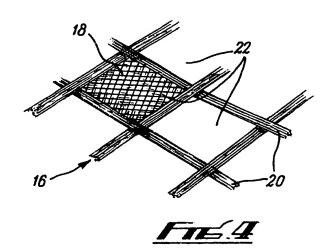
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# INTERNATIONAL SEARCH REPORT

Int. Itional Application No PCT/GB 98/01270

A. CLASSII IPC 6	FICATION OF SUBJECT MATTER B29C43/36 B29C33/40 B30B15/06	//B29K21:00,B29K10	5:10		
Accoming to	International Patent Classification(IPC) or to both national classification	on and IPC			
B. FIELDS					
	cumentation searched (classification system followed by classification B29C B29D B30B	symbols)			
Documentat	non searched other than minimumdocumentation to the extent that suc	n documents are included in the fields sear	Relevant to claim No.  1-24  20,22-24  1,2,5,6,8,9,11-13,17-19,21  20,22-24  1,2,5,6,8,9,11-13,17-19,21  annex.  Innex.  Innex identification but application		
Electronic da	ata base consulted during the international search (name of data base	and, where practical, search terms used)			
C. DOCUME	ENTS CONSIDERED TO BE RELEVANT				
Category '	Citation of document, with indication, where appropriate, of the relev	ant passages	Relevant to claim No.		
Х	US 4 770 928 A (GAWOROWSKI ANDREW AL) 13 September 1988 see the whole document	J ET	1-24		
Х	EP 0 318 415 A (UNITED TECHNOLOGI)	ES CORP)	20,22-24		
Α	see the whole document		8,9, 11-13,		
х	EP 0 491 646 A (UNITED TECHNOLOGI 24 June 1992	ES CORP)	20,22-24		
А	see column 6, line 37 - column 9, claims; figures	line 9;	8,9, 11-13,		
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X Furt	ther documents are listed in the continuation of box C.	Patent family members are listed in	s annex.		
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## INTERNATIONAL SEARCH REPORT

Inst. ional Application No PCT/GB 98/01270

	ation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category :	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4 824 631 A (YEAGER JAMES F) 25 April 1989 see the whole document	1,5,6,8, 9,22-24
A	US 3 990 930 A (SCHMIT GEORGES) 9 November 1976	1,2,5,6, 11,12, 17,18, 20-24
	see the whole document	20-24
A	US 5 324 376 A (WEIMER RUSSELL ET AL) 28 June 1994	1,2, 11-13, 20,22-24
	see column 2, line 49 - column 4, line 39; claims 7-14; figures	23,22 2
A	EP 0 491 651 A (UNITED TECHNOLOGIES CORP) 24 June 1992	1,2,9, 11-13, 20-24
	see the whole document	20 24
A	EP 0 572 248 A (BRITISH AEROSPACE) 1 December 1993 see column 4, line 19 - column 5, line 19; claims; figures	1,22-24
A	GB 2 290 742 A (ADVANCED COMPOSITES GROUP LTD) 10 January 1996 see the whole document	1,2,12, 20,22-24
	<del></del>	

# INTERNATIONAL SEARCH REPORT

Information on patent family members

PCT/GB 98/01270

			1	
Patent document cited in search report	,	Publication date	Patent family member(s)	Publication date
US 4770928	Α	13-09-1988	EP 0342286 A DE 3888679 D DE 3888679 T	23-11-1989 28-04-1994 03-11-1994
EP 0318415	Α	31-05-1989	JP 1069637 A US 5071338 A US 5217669 A	15-03-1989 10-12-1991 08-06-1993
EP 0491646	Α	24-06-1992	US 5152949 A CA 2054066 A DE 69109255 D DE 69109255 T JP 4294113 A	06-10-1992 20-06-1992 01-06-1995 24-08-1995 19-10-1992
US 4824631	Α	25-04-1989	NONE	
US 3990930	Α	09-11-1976	NONE	
US 5324376	Α	28-06-1994	US 5250142 A	05-10-1993
EP 0491651	A	24-06-1992	US 5126092 A CA 2056330 A DE 69111775 D DE 69111775 T JP 4301410 A US 5286438 A	30-06-1992 20-06-1992 07-09-1995 11-01-1996 26-10-1992 15-02-1994
EP 0572248	Α	01-12-1993	NONE	
GB 2290742	Α	10-01-1996	AU 2748995 A . WO 9600642 A	25-01-1996 11-01-1996